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A NON-CONVENTIONAL BIODIESEL PROCESS ROUTE FROM WASTE PALM FATTY ACID DISTILLATE AND ETHYL ACETATE VIA ESTERIFICATION

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Abstract

The high cost and food competition associated with conventional biodiesel feedstocks limit its widespread adoption. This research investigates using Palm Fatty Acid Distillate (PFAD), a low-cost industrial by-product which is high in Free Fatty Acids (FFAs), as a sustainable feedstock. A novel glycerol-free esterification route was developed employing ethyl acetate as acyl acceptor and sulfuric acid as catalyst, producing fatty acid ethyl esters (FAEEs) and valuable acetic acid as by-product. The characterization of PFAD confirmed its high FFA content of 91.78±0.62 %, then the Taguchi method was employed to systematically optimize key reaction parameters: reaction time (2–4 h), temperature (55–75 °C), catalyst amount (3–9 wt%), and ethyl acetate to PFAD molar ratio (5:1–15:1). Taguchi orthogonal design revealed that the ethyl acetate to PFAD molar ratio had the most significant impact on FFA conversion and time had the lowest impact. Optimal conditions were identified as 4 h, 65 °C, 6 wt%, and 15:1 molar ratio, yielding a predicted maximum FFA conversion of 87.74 %. Experimental validation under these conditions achieved an average conversion of 86.28, confirming excellent agreement with the prediction. This research presents one of the first systematic Taguchi optimizations of PFAD esterification using ethyl acetate, offering a greener, glycerol-free pathway compared to conventional methanol-based processes. The proposed route contributes to sustainable biodiesel production from waste products, aligning with global renewable energy goals and economic viability.

Keywords: Energy, Free fatty acid, Ethyl acetate, Palm fatty acid distillate, Taguchi.

Introduction

Energy is the backbone of all production activities and is vital in driving development processes across various sectors. Without energy, production activities would come to a standstill, highlighting its indispensable nature in the functioning of economies and societies [1]. Global energy consumption is projected to continue increasing for several generations due to ongoing industrialization, urbanization, and population growth. However, the human energy production is the primary source of green-house gas emissions into the atmosphere, primarily through the combustion of fossil fuels. Among the combustion products of fossil fuels, carbon dioxide (CO_2) is the most prevalent green-house gas, characterized by its colorless and odorless nature [2]. The extraction, processing and burning of fossil fuels have detrimental effects on the environment, posing a threat to numerous plant and animal species, potentially driving them to extinction [3]. If the escalating fossil fuel consumption trend persists, humanity could face extinction because fossil fuels are finite. This basis highlights the urgent need to transition away from fossil fuels as our primary energy source [4].

The rising interest in renewable energy is partly due to growing worries about environmental pollution, resource depletion, and the potential impacts of climate change from ongoing dependence on traditional fossil and nuclear fuels [5]. According to the Intergovernmental Panel on Climate Change (IPCC), the energy sector accounts for approximately 73 % of global green-house gas emissions, underscoring the urgent need to transition to low-carbon alternatives [6]. The growth in energy demand necessitates the search for environmentally friendly, economically, viable and readily available alternatives to fossil fuels due to depletion of petroleum reserves and growing environmental concerns. Renewable energy sources, such as solar, wind, hydroelectric, and biofuels, are central to this transition, offering pathways to decarbonize energy systems while ensuring energy security and sustainability. Among these, biodiesel stands out as a vital bridge in global transition to a sustainable energy future [7].

Biodiesel is a renewable source of energy produced from different vegetable oils, animal fats and greases. Both the plant and animal feedstocks undergo conversion process in order to produce a suitable fuel for running the diesel engines [8]. The versatile production method allows for the transformation of various feedstocks into a sustainable and renewable fuel alternative, contributing to the diversification of energy sources and reducing reliance on conventional fossil fuels [9]. The price of feedstock significantly influences the total cost of biodiesel production with different feedstock oils having varying effects on its price. However, the widespread adoption of biodiesel is hindered by the high cost of conventional feedstocks, such as refined vegetable oils, which compete with food resources and exacerbate land-use conflicts [10]. To address these challenges, researchers have increasingly turned to low-cost, non-edible feedstocks, particularly industrial by-products, which align with circular economy principles by converting waste into value-added products. Although waste food materials often consist of high free fatty acid content which needs to be reduced before use, the fatty acid methyl esters obtained are similar to those derived from edible oils [11].

Palm Fatty Acid Distillate (PFAD) is a by-product of the palm oil refining process, specifically derived from the distillation of crude palm oil, making it readily available in palm oil producing regions such as Southeast Asia and parts of Africa. Its consistent supply is largely dependent on global palm oil production volumes, which remain high due to the extensive demand for edible oils and oleochemicals. Economically, PFAD is a low-cost feedstock compared to refined vegetable oils, as it is considered a secondary product of the refining process. The cost advantage enhances its attractiveness for biodiesel production and other value-added applications. It consists mainly of free fatty acids (FFAs) and traces of other components such as sterols, squalene, vitamin E, and glycerides [12,13]. The physical refining process, which involves heating the oil to high temperatures to eliminate impurities and then distilling the fatty acids to separate them from the more refined oil, is usually when PFAD is gotten. This process helps to enhance esterification efficiency and reduce emissions of green-house gases. As a by-product, PFAD is sometimes viewed as more sustainable than primary palm oil products, with life-cycle assessments showing up to 86.5% lower GHG emissions for PFAD-based biodiesel if classified as a residue rather than a co-product and this process aligns with SDG-12 (Responsible Consumption and Production) [14,15]. However, high FFA content of PFAD poses a major obstacle to the conventional base-catalyzed transesterification process, as FFAs react with basic catalysts to form soaps which also reduces the biodiesel yield and complicates purification [16]. Also, the over-supply of glycerol from methanol caused a drastic drop of the value in the market which also poses threats to the environment in terms of disposal and this has led to the interest in other viable options [17].

Acid-catalyzed esterification is a good alternative that offers a viable alternative, enabling the direct conversion of FFAs into fatty acid methyl esters (FAMEs). Sulfuric acid, a low-cost and highly efficient homogeneous catalyst, is particularly effective in protonating FFAs [18,19]. Ethyl acetate acts as an acyl acceptor, reacting with Free Fatty Acids (FFAs) in PFAD to form Fatty Acid Ethyl Esters (FAEEs) and acetic acid as a by-product, thereby eliminating the glycerol formation. Unlike methanol, ethyl acetate is less toxic, more biodegradable, and thermally stable under acidic conditions, whereby, the by-product (acetic acid) is useful in food, pharmaceutical and cosmetic industries [20].

Conventional methanol-based processes typically achieve 90–98% FAME yield but generate large quantities of glycerol which has been found helpful over the years for mostly industrial purposes before biodiesel started. However, the market value has collapsed due to oversupply which has become a significant drawback in biodiesel production, causing the improper disposal of excess glycerol and its separation process to become an important environmental concern [14]. Although ethyl acetate is more expensive than methanol or ethanol, this acyl acceptor enables a glycerol-free process, thereby reducing purification steps and downstream costs. The by-product (acetic acid) can be recovered and sold to manufacturing industries such as food, cosmetics and pharmaceuticals, partially compensating for the higher reagent cost. The lower toxicity and better environmental profile make it suitable for sustainable and green biodiesel production. The formation of acetic acid also contributes to a circular bioeconomy by providing an additional value stream and lowering disposal concerns [21].

However, several studies have reported the use of ethyl acetate in transesterification and interesterification reactions for biodiesel synthesis, only limited studies to the best of our knowledge have focused on its application with Palm Fatty Acid Distillate (PFAD) under systematic optimization [22]. Hence, this research contributes by employing the Taguchi orthogonal design to optimize PFAD esterification using ethyl acetate, highlighting process efficiency and environmental benefits.

In contrast to other optimization methods, Taguchi design as a systematic, statistically robust, and cost-efficient optimization framework that identifies the most influential reaction parameters (time, temperature, catalyst loading, and ethyl acetate: PFAD molar ratio) with minimal experiments. Taguchi optimization method is highly significant as a statistical design of experiments that provides a systematic framework to evaluate multiple variables simultaneously with minimal experimental trials [23]. By using orthogonal arrays and signal-to-noise ratio (SNR), the Taguchi method identifies optimal conditions while accounting for variability making it a powerful tool for industrial processes requiring reproducibility and scalability. This approach not only enhances process efficiency but also reduces time and costs, aligning with the economic and environmental goals of sustainable biodiesel production [24]. Therefore, this research aims to investigate the synthesis of biodiesel through esterification of free fatty acids in palm fatty acid distillate with ethyl acetate in the presence of homogeneous sulfuric acid catalyst, thereby, the novelty of this research is the esterification of palm fatty acid distillate which is considered as a sustainable feedstock in the production of biodiesel alongside ethyl acetate instead of using methanol or dimethyl carbonate, thereby making this route glycerol-free in the presence of sulfuric acid catalyst, optimized through Taguchi method.

Results and discussion

Physicochemical characterization of PFAD

Free fatty acid value indicates the level of free fatty acid in the feedstock. The determination of FFA content is an important analysis for assessing the quality of the oil, as well as monitoring their degradation [25]. The FFA value of PFAD was reported in this research to be 91.78±0.62 %. The FFA content of PFAD in this research was found slightly higher than 87.04±0.1 % which is the FFA value of PFAD reported in Jumaah et al. [26]. However, this high value of FFA in both feedstocks suggest significant hydrolysis of triglycerides during the deodorization process which makes it suitable for producing biodiesel.

Acid value is a key parameter that monitors the level of corrosiveness of the feedstock, so as to know whether it will require neutralization process to reduce the acidity. This determines the quality of biodiesel produced [27]. High acid value indicates the presence of unreacted FFAs, which can promote metal corrosion during fuel storage and engine use. The acid value obtained in this research (234.82±1.65 mg KOH/g) was reduced significantly after esterification, indicating successful conversion of FFAs to esters and improved fuel stability. Comparative data from other studies show that biodiesel with acid value below 0.5 mg KOH/g meets ASTM D6751 and EN 14214 standards for corrosion resistance [28, 29]. However, the high acid value contained in the feedstock reported in this research confirmed that they contain greater amounts of free fatty acids and require pretreatments before the production of biodiesel.

Iodine value is an important property that shows the unsaturation level (that means the total number of double bonds) in the oil samples. The iodine value of PFAD in this research which is 0.50±0.04 g I_2/100g, and is still within the standard value. Laghari et al. [30] reported the iodine value of SODD to be 109±1.23 and 110±2.41 g I_2/100g respectively which are close to the standard value. Although the values are way higher than iodine value of the two feedstocks obtained in this research. The standard iodine value for biodiesel production was 120 g I_2/100g for Europe’s EN 14214 specifications [31]. The iodine value obtained in this research is lower than that of Jatropha oil seed obtained in Yadav et al. [32] which is 109.79 g I_2/100g.

Saponification value is an index that shows the amount of potassium hydroxide (KOH) needed to saponify the oil and it also estimates the average molecular weight of the fatty acid present in the oil. A high saponification value indicates a low average fatty acid and low saponification value suggests superior quality [33]. The saponification value of PFAD obtained in this research was reported to be 164.58±1.31 mg KOH/g. Eze [34] reported the saponification value of Bambara groundnut seed oil to be 157.4 mg KOH/g which was lower than the saponification value of PFAD in this research. However, the saponification value of used red palm oil reported by Chie-

Amadi et al. [35] was found to be slightly higher the saponification value of PFAD in this research.

Peroxide value indicates the extent of oxidation (that means how oxidized the oil is) affecting the flavor, color and shelf life. The higher the peroxide value, the more exposed it is to deterioration which also affects the oil's shelf life [36]. The peroxide value for PFAD in this research was 26.47±0.01 meq O_2/kg. The peroxide value for PFAD in this research was found to be similar to the result reported in Esan et al. [37], which the peroxide value of PFAD was 26.30±0.01 meq O_2/kg. The results confirmed PFAD as ideal feedstock in biodiesel production which also helps in waste management. Reported GC analysis showed PFAD to be dominated by palmitic (47.51%), oleic (38.69%), linoleic (9.04%) and stearic (4.76%) acids, corresponding to a calculated average molecular weight of 260.17 g/mol [38]. Table 1 reveals the physicochemical properties of PFAD crude palm oil, thereby confirming the suitability of PFAD in the synthesis of biodiesel.

Table 1: Comparative Physicochemical Properties of PFAD and Crude Palm Oil

Physicochemical Property	Palm Fatty Acid Distillate (PFAD) [This study]	Crude Palm Oil [39]
Free fatty acid value (%)	91.78±0.62	0.524-0.956
Acid value (mg KOH/g)	234.82±1.65	1.047-1.911
Iodine value (g I_2/100 g)	0.50±0.04	40.61-57.739
Saponification value (mg KOH/g)	164.58±1.31	199.59-207.57
Peroxide value (meq O_2/kg)	26.47±0.01	2.43-4.01

Esterification reaction of Palm Fatty Acid Distillate (PFAD)

In this research, the Taguchi L9 experimental design was used to optimize the production of biodiesel from Palm Fatty Acid Distillate (PFAD) and ethyl acetate through esterification reaction.

Optimization of the reaction conditions using Taguchi orthogonal design

The results, including the percentage of FFA Conversion and signal-to-noise ratio (SNR) values, are presented in Table 2. The primary aim was to identify optimum reaction conditions for achieving the highest FFA conversion. Using Minitab 19® software with the Larger-the-better model for SNR analysis, it was found that experiment 4 yielded the highest FFA conversion of 87.81 %, while experiment 1 resulted in the lowest conversion of 77.92 %. Although experiment 4 gave the maximum FFA conversion, the reaction conditions in this experiment are not the accurate optimum conditions. Therefore, the signal-to-noise ratio level (SNRL) was used to achieve accurate optimum reaction conditions. For parameter A (Time) at level 1, the SNRL was calculated from the SNR values of experiment 1, 2, 3 to give 38.46 and the SNRL values of parameter A at level 2 and 3 were obtained from the SNR values of experiment 4, 5, 6 and 7, 8, 9 to be 38.69 and 38.71.

For parameter B (Temperature) at level 1, the SNRL was calculated from the SNR values of experiment 1,4,7 to be 38.45. The SNRL value of parameter B at level 2 and 3, were obtained from the SNR values of experiment 2, 5, 8 and 3, 6, 9 to be 38.73 and 38.68 respectively. The SNRL value for parameter C (Catalyst amount) at level 1 was calculated from the SNR values of experiment 1,6,8 to be 38.39. For level 2 and 3, the SNRL values of parameter C were calculated from SNR values of experiment 2, 4, 9 and 3, 5, 7 to be 38.75 and 38.72 respectively. The SNRL value for parameter D (ethyl acetate to PFAD ratio) at level 1 was calculated from the SNR values of experiment 1, 5, 9 to be 38.39. For level 2 and 3, the SNRL values of parameter D were calculated from the SNR values of experiment 2, 6, 7 and 3, 4, 8 to be 38.63 and 38.84 respectively.

Table 3 presents the SNRL values of each parameter at different levels along with the difference in signal-to-noise ratio level (DSNRL) of each parameter as obtained and the rank assigned to each factor. The DSNRL which is also referred to as the delta in Table 3 is calculated by subtracting the lowest SNRL from highest SNRL for each parameter, the rank of each parameter is arranged based on DSNRL values ranging from maximum to minimum in order of 1-4, a higher Delta value indicates a greater effect of that parameter on the FFA conversion. The rankings which are determined by the delta value indicated that ethyl acetate to PFAD molar ratio had the most substantial impact on FFA conversion, followed by catalyst amount and the temperature in that order. In contrast, reaction time had the least influence on FFA conversion.

Table 2: PFAD FFA conversion yield, SNR and SNR_T for the nine experimental runs

Runs	Time (h)	Temp. (°C)	Catalyst amount (wt.%)	EA to PFAD Molar ratio	FFA Conversion (%)	SNR
1	2.00	55.00	3.00	5:1	77.92	37.83
2	2.00	65.00	6.00	10:1	86.20	38.71
3	2.00	75.00	9.00	15:1	87.54	38.84
4	3.00	55.00	6.00	15:1	87.81	38.87
5	3.00	65.00	9.00	5:1	85.79	38.67
6	3.00	75.00	3.00	10:1	84.35	38.52
7	4.00	55.00	9.00	10:1	85.55	38.64
8	4.00	65.00	3.00	15:1	87.26	38.82
9	4.00	75.00	6.00	5:1	85.87	38.68
SNR_T-Overall mean						38.35

Table 3 illustrates the relation of SNRL with the influence of each parameter at three different levels on FFA conversion. The SNRL value directly correlates with the influence of a specific parameter at a given level on the FFA conversion; hence, higher SNRL value indicates a higher influence of that parameter at that level. This shows that the maximum reaction condition required to achieve the optimal FFA conversion is determined by the highest SNRL value for each parameter depicted in Table 3.

Table 3: SNRL values of each parameter at different levels and rank of parameters for PFAD FFA Conversion

Level	Time	Temperature	Catalyst amount	Ethyl acetate to PFAD ratio
1	38.46	38.45	38.39	38.39
2	38.69	38.73	38.75	38.63
3	38.71	38.68	38.72	38.84
Delta	0.25	0.28	0.36	0.45
Rank	4	3	2	1

The optimum FFA conversion yield from the esterification of PFAD using ethyl acetate was obtained from the optimum reaction conditions which are time at level 3 (4 h), temperature at level 2 (65 ^{o}C), catalyst concentration at level 2 (6 wt%), and ethyl acetate to PFAD molar ratio at level 3 (15:1). The Taguchi method was selected because it requires fewer experimental runs (9) while still effectively identifying the main effects and optimal conditions efficiently. This approach significantly reduced experimental cost, time, and material waste compared to

Response Surface Methodology (RSM) which requires 31 runs, thereby exceling in quadratic modeling but assumes prior knowledge of interactions or minimum factorial experimental designs which is 28-30 runs. Moreover, the use of signal-to-noise (SNR) ratios allows effective quantification of parameter sensitivity and robustness under variable conditions which is ideal for initial optimization in biodiesel processes unlike other methods [23, 24].

Statistical analysis of data variance

The influence of each reaction parameter was evaluated statistically by the analysis of variance, whereby the percentage contribution of each parameter was also determined. The results, summarized in Table 4, revealed that the SS_K values indicate the relative impact of each parameter and the values were calculated using equation (15). According to the SS_K values and percentage contribution of the parameters calculated, ethyl acetate to PFAD ratio had the most significant influence, while reaction time had the least impact on the FFA conversion. Specifically, the percentage contributions were calculated as 28.10 % for ethyl acetate to PFAD molar ratio and 22.59 % for reaction time.

Table 4: Percentage contribution of each parameter for PFAD FFA conversion

Parameters	**SS_K**	**Percentage contribution**
Reaction time	0.2573	22.59
Reaction temperature	0.2633	23.11
Catalyst amount	0.2985	26.20

EA to PFAD molar ratio	0.3201	28.10

SS_K is the sum of squares for the K_{th} factor

Additionally, catalyst amount and reaction temperature contributed 26.20 % and 23.11 % respectively. The ranking of these parameters based on percentage contribution aligned with the order present in Table 3. Furthermore, it has been established that ethyl acetate achieves high biodiesel yields at temperatures exceeding its boiling point (higher temperatures), necessitating specialized reactors to prevent the evaporation of ethyl acetate while maintaining the required molar ratio. For instance, biodiesel yields of 99 %, >60 %, 91.80 %, and 95.26 % have been reported at temperatures above 110 ^{o}C using Palm oil, dry microalgae, Spent Coffee grounds (SCGs), and, leftover cooking oil respectively [20, 40, 41, 42].

Main effect plots of FFA conversion in PFAD to biodiesel

Fig. 1 shows the average FFA conversion at each level of the factors whereby the plot identifies the parameter that have the most significant impact on FFA conversion and the optimal levels of each parameter to maximize conversion. The plot illustrates an increasing trend in FFA conversion as time and ethyl acetate to PFAD molar ratio increases, it suggests that longer reaction times and ethyl acetate to PFAD molar ratio favor higher conversion but ethyl acetate to PFAD molar ratio had the highest influence which indicates that a larger excess of ethyl acetate improves FFA conversion. For temperature and catalyst amount above 65 ^{o}C and 6 wt% shows these parameters influence the decrease of the FFA conversion beyond those conditions. Fig. 1 shows the FFA conversion yield at each parameter across various levels and ethyl acetate to PFAD molar ratio has proven to have the highest impact on the FFA conversion yield.

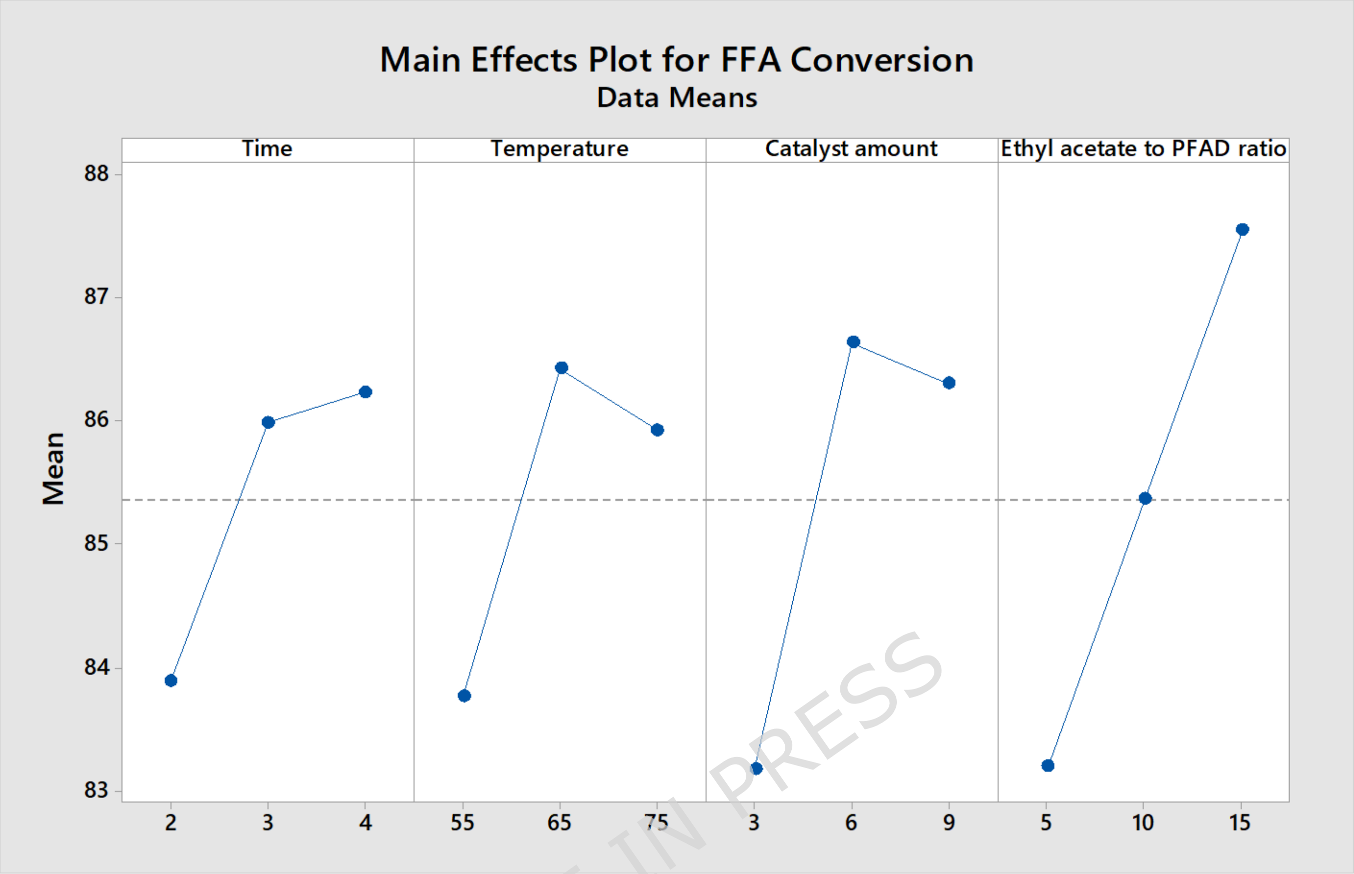

Fig. 1: FFA conversion of PFAD at three different levels of each parameter

Influence of the reaction parameters on the yield of PFAD FFA conversion

The influence of each reaction parameter on the FFA conversion from the esterification of PFAD was illustrated in the contour plots of Fig. 2 (a-f) and these reaction parameters include; time (2, 3, 4 h), temperature (55, 65, 75 ^{o}C), catalyst concentration (3, 6, 9 wt%) and ethyl acetate to PFAD molar ratio (5:1, 10:1, 15:1). These selected values for each parameter were determined from initial experimental study, correlating with this research aim to maximize the FFA conversion yield from esterification of PFAD using ethyl acetate via Taguchi method.

The contour plot in Fig. 2 (a) reveals the relationship between temperature and reaction time, indicating that higher temperatures generally lead to increase in FFA conversion yield.

Observations showed that between 2.75-4 h, the yield of FFA conversion increased to above 86 % which indicates that longer reaction time may allow for more complete conversion and it can also lead to diminishing returns after a certain point [43]. Thereby the yield decreased as the temperature approached 75 ^{o}C and above, which is as a result of thermal decomposition of fatty acid ethyl esters [44]. The time in this research is in alignment with Aliyu et al. [31], whereby the duration higher than 4 h caused a drastic drop in the FAME yield.

Observations from the contour plot in Fig. 2 (b) shows the impact of catalyst concentration and time on the conversion process of FFA which illustrates the increase in FFA conversion yield as the catalyst concentration and time is increased. Although as the catalyst amount approached 6 wt% and the time approached 3.5 h, the FFA conversion remained constant at above 86 % showing how relatively time and catalyst amount are intertwined in achieving optimum FFA conversion. However, this can be associated to the need for a sufficient amount of catalyst to reduce the activation energy required to reach equilibrium [45]. Hence, the reaction time in this research is consistent with Esan et al. [46], which reported the FFA conversion yield to be 89.32 % at reaction time of 3 h, catalyst amount of 12 wt% and decrease was noticed in the FFA conversion yield at a reaction time beyond 3 h.

The influence of ethyl acetate to PFAD molar ratio and temperature on the FFA conversion yield is displayed on the contour plot of Fig. 2 (c). It was noted that the FFA conversion increased slowly but at ethyl acetate to PFAD molar ratio of >10:1, optimum FFA conversion was attained above 86 % at any given temperature. This ratio is necessary to adequately esterify the significant amount of free fatty acid present in PFAD and lower FFA conversion observed between 5:1 and 10:1 which are likely due to the insufficient ethyl acetate for the esterification of PFAD. However, the elevated temperature also increased the reaction rates, thereby causing increase in the FFA conversion between 66 and 74 ^{o}C. The 15:1 ethyl acetate to PFAD molar ratio in this research is similar to that reported by Yaakouby et al. [47], whereby the optimum PFAD/methanol molar ratio for maximum FAME yield is 1:15. A maximum FAME yield of 93.7 % was reported by Hazmi et al. [14] under the optimum reaction condition of 1:19, time of 83.7 ^{o}C, 1.16 h and 2.2 wt% of catalyst loading, the temperature is high because of the short reaction time in order to produce optimum FAME yield.

Fig. 2 (d) illustrates the contour plot of ethyl acetate to PFAD molar ratio and time in relation to FFA conversion. From the plot, the ethyl acetate to PFAD ratio has greater impact on the optimum FFA conversion yield in comparison to the reaction time, whereby this result shows the optimum FFA conversion yield of above 86 % at ethyl acetate to PFAD ratio of 10:1 with regards to any given time and this molar ratio is in alignment with that in Fig. 2 (c). This finding also aligns with research of Wong et al. [48], who investigated the feasibility of waste banana peel and empty fruit bunch in synthesizing high performing heterogeneous catalyst. They observed that increasing the methyl acetate to oleic acid molar ratio led to higher biodiesel yield with an optimal ratio of 50:1 achieving a 52.3 % yield. An optimal time frame was identified where the FFA conversion yield peak on the plot but further increase in time cause decrease in the conversion yield which shows that the reaction has gotten to the unfavorable time for the conversion yield. Since esterification process is reversible and requires prolonged reaction times along with increased molar ratios of ethyl acetate to PFAD, this ensures adequate time for ethyl acetate to effectively drive the reaction towards product formation [31].

The contour plot in Fig. 2 (e) depicts the relationship between catalyst amount and temperature, indicating how these variable affects the conversion of free fatty acids in the reaction process. Higher FFA conversion rates are generally observed with optimal catalyst amounts and temperatures. The data suggests that increasing the catalyst amount tends to enhance the FFA conversion, particularly at elevated temperatures, which may facilitate better reaction kinetics. The optimum conversion yield of FFA was achieved at catalyst concentration between >5 and <9 wt% and temperature between 62.5 and 73 ^{o}C. However, due to excessively high temperature above 73 ^{o}C and high catalyst above 9 wt% as shown in this plot, the degradation of sensitive compounds occurred thereby causing reduction in the conversion yield of FFA which decreases the catalyst performance [49]. This is consistent with Da Luz et al. [43] that obtained its highest FFA conversion above 75 % at 3-4 wt% of the catalyst and increasing the catalyst above 6 wt% did not significantly increase the FFA conversion.

The contour plot displayed in Fig. 2 (f) demonstrates the interaction between the catalyst amount and ethyl acetate to PFAD molar ratio, highlighting their combined effect on FFA conversion rates. Higher conversion rates are typically achieved with specific combinations of these parameters. As shown in this plot, increase in the catalyst amount leads to improved FFA conversion and this is also visible in Fig. 2 (a) and 2 (e), thereby suggesting that a higher catalyst concentration enhances the reaction efficiency. According to Le Chatelier’s principle, the equilibrium can be shifted towards the product by either using an excess of one reactant or continuously removing one of the products during the reaction [42]. The conversion yield increased from 78 % to 86 % within 5:1 to 10:1 ethyl acetate to PFAD molar ratio together with catalyst amount of 3-8.5 wt% and the maximum conversion yield was attained when the ethyl acetate to PFAD molar ratio was >1:12. This trend was in accordance with Yaakouby et al. [50] whereby optimum FFA conversion was observed at PFAD to methanol molar ratio of 1:15, catalyst of 5 wt%, time duration of 3 h and temperature of 80 ^{o}C, a significant decrease was noticed in the FFA conversion at the reaction condition above them.

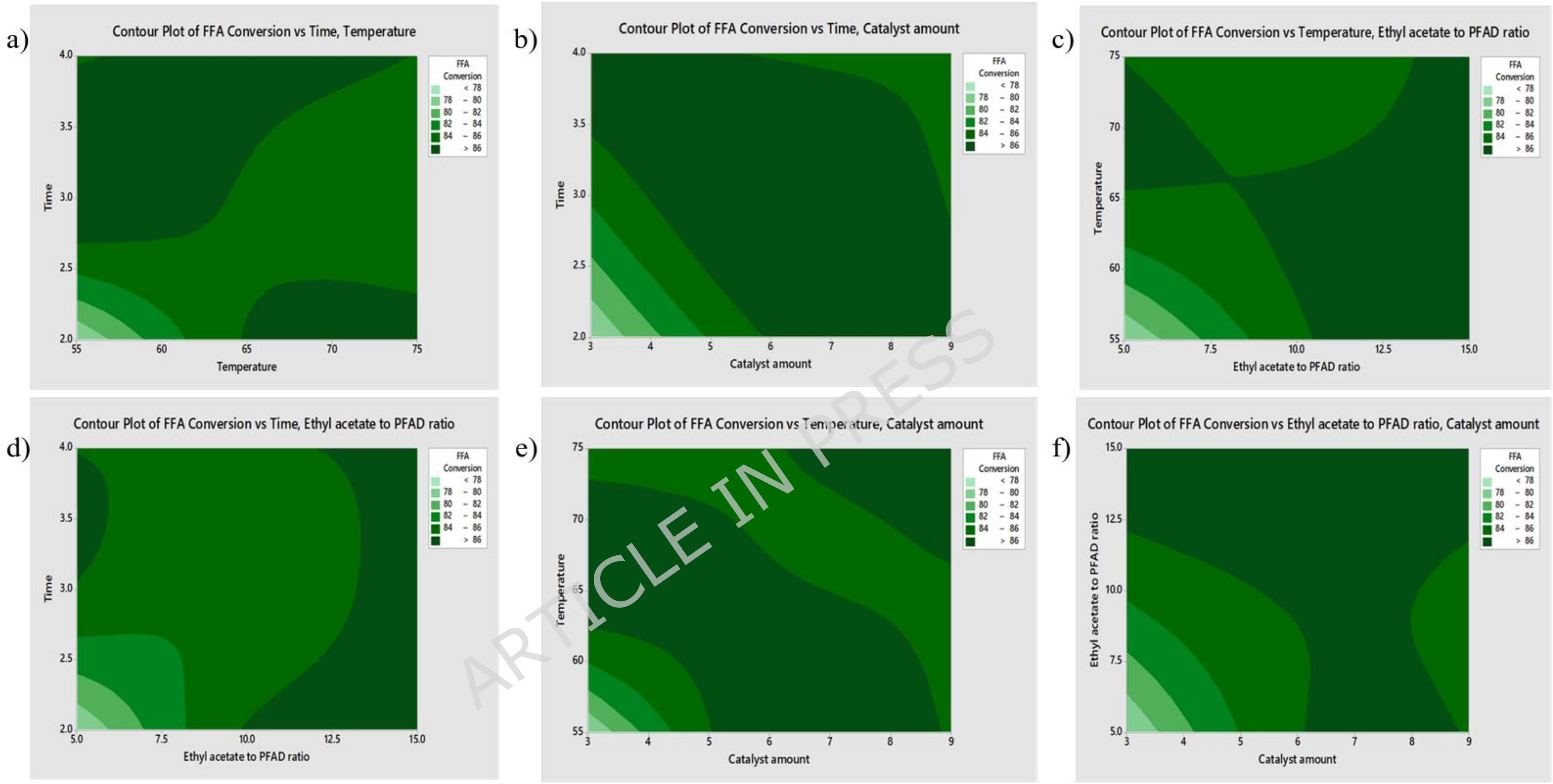

Fig. 2: Contour plot of PFAD FFA conversion with (**a**) time and temperature, (**b**) time and catalyst amount, (**c**) temperature and ethyl acetate to PFAD ratio, (**d**) time and ethyl acetate to PFAD ratio, (**e**) temperature and catalyst amount, (**f**) ethyl acetate to PFAD ratio and catalyst amount

Interaction plots of PFAD FFA conversion.

The interaction plot of FFA conversion in Fig. 3 (a) illustrates how temperature and time jointly affect FFA conversion yields. The FFA conversion increases with both temperature and time, but the rate of increase varies depending on the interaction between these two parameters. At lower temperatures (55 ^{o}C), the FFA conversion is relatively lower, indicating that heat plays a crucial role in improving the reaction efficiency and as the temperature increases across 65 and 75 ^{o}C, even shorter reaction times (2 h) achieve high conversion yield. It was observed that at 3 h, there was substantial decrease in the FFA conversion across various temperatures which indicates that longer time can effectively decrease the FFA conversion. This interaction plot indicates that the effect of temperature is dependent on the level of time, and the change in FFA conversion is higher in 2 h than 3-4 h which means that the reaction reaches higher FFA conversion more quickly at 2 h when the temperature is increased. At longer time (4 h), the increase in FFA conversion becomes less pronounced, indicating a decrease in the possible plateau effect where further heating leads to thermal decomposition and this is in accordance with Kusumaningtyas et al. [51] whereby the FFA conversion began to decline at a temperature of 50 ^{o}C for 5 h which also causes damage to the catalyst. The optimal conditions for maximizing FFA conversion in this plot is a temperature of 55 ^{o}C at 3 h, whereby using a higher temperature with a slightly higher time may yield nearly the same result. The time in this research is similar to that reported by Kedir & Asere [52] where sulfonated catalyst of 4 wt% produced optimum biodiesel yield of 82 % at a time not longer than 4 h.

Fig. 3 (b) displays the interaction plot of the influence of catalyst amount and time on the FFA conversion yield. From the plot, the effect of catalyst on the FFA conversion is more visible between 3 and 6 wt% and the effect of time on the FFA conversion is between 2 and 3 h where the FFA conversion substantially increased between those durations. Although, the effect of the catalyst depends on time and the change in catalyst concentration is bigger in shorter time (2 h) than longer time (3 and 4 h). This also proves that time has significant effect with catalyst between 2 and 3 h than 3 and 4 h on the FFA conversion yield. According to this plot, the maximum FFA conversion yield is achieved at the time of 3 h and catalyst of 6 wt%. Therefore, further increase in the time and catalyst will cause a drop in the FFA conversion yield as shown in the plot whereby there was great decrease across the different duration at 9 wt%. The influence of catalyst activity with methyl acetate was investigated in Ketzer et al. [53] and the optimum was reported to be 10 wt% which yielded maximum conversion of 79.4 %. Ibrahim et al. [54] reported a maximum conversion of 96 % with optimal reaction conditions of impregnated sulphonated catalyst of 2 wt% with a duration of 4 h which was similar to this research.

The interaction plot for FFA conversion yield with ethyl acetate to PFAD molar ratio and time as displayed in Fig. 3 (c) helps to understand how these two factors influence the efficiency of the reaction. From the plot, it is noted that increasing the ethyl acetate to PFAD molar ratio enhances the FFA conversion at 2 h, whereby the reaction reversibility makes it essential to use excess ethyl acetate to drive the reaction forward toward the desired ester product [55]. However, beyond 15:1, further increases may not significantly improve conversion due to saturation effects. Longer time leads to higher FFA conversion which suggests that time allows for more complete esterification leading to improved yield. However, after 3 h, the increase in conversion slows down, indicating a potential reaction equilibrium. Therefore, the effect of ethyl acetate to PFAD molar ratio is more pronounced at 2 h but conversion yield is not significantly improved at 5:1 unlike 15:1 regardless of the reaction time which means the excess ethyl acetate compensates for shorter durations. This suggests that an optimum FFA conversion yield is achieved at 3 h and 15:1 respectively. Similar observation was reported by Buchori et al. [56], such that methanol to PFAD molar ratio of 16:1 at a longer duration of 6 h produced a biodiesel yield of 94.915 %.

The interaction plot represented in Fig. 3 (d) shows the impact of temperature and ethyl acetate to PFAD molar ratio on FFA conversion yield. There is significant increase in FFA conversion yield with increase in temperature across various ethyl acetate to PFAD molar ratios, thereby causing increase in the molecular activity and accelerating the reaction kinetics. Although, 10:1 is more responsive to temperature changes with significant increase in FFA conversion compared to 5:1, whereby 10:1 shows higher increase in FFA conversion yield with increasing temperature, this also proves that ethyl acetate to PFAD molar ratio has significant effect with temperature between 5:1 and 10:1 than 10:1 and 15:1. Although, there was a drop at 10:1 with 75 ^{o}C but substantial increase was noticed at 15:1 at the higher temperature of 75 ^{o}C. The effect of temperature on the FFA conversion was more significant at 55 and 65 ^{o}C and this confirms that at higher temperature (75 ^{o}C), the conversion yield does not significantly improve. Same trend for best result was reported by Al-Hamamre et al. [57], which optimum reaction temperature of 65 ^{o}C produced maximum conversion yield of about 100 % at the duration of 2 h. Rathnam et al. [40] optimized the production of biodiesel from microalgae using non-catalytic transesterification at a molar ratio of 15:1 giving conversions above 60 %.

The interaction plot for catalyst concentration and ethyl acetate to PFAD molar ratio on FFA conversion in Fig. 3 (e) provide insights on how these parameters influence the conversion yield. The main effect of catalyst on the conversion yield is between 3 and 6 wt%, which means the difference in conversion between 6 and 9 wt% catalyst is smaller than between 3 and 6 wt%, thereby causing diminishing returns at higher catalyst concentrations [58]. At catalyst concentration of 3 wt%, increasing the ethyl acetate to PFAD molar ratio significantly improves the conversion but at higher catalyst concentration of 9 wt%, the effect of ethyl acetate to PFAD molar ratio is present but less pronounced. Therefore, the best conditions for maximizing FFA conversion in this plot involved catalyst concentration of 6 wt% and ethyl acetate to PFAD molar ratio of 15:1.

The influence of catalyst concentration and temperature on FFA conversion were investigated by varying the catalyst concentration from 3 to 9 wt% and temperature between 55 and 75 ^{o}C in the interaction plot displayed in Fig. 3 (f). This plot shows strong interaction effect between the catalyst amount and temperature and the increase in conversion yield is more substantial with higher catalyst concentration which suggests a strong synergistic effect between temperature and catalyst amount. At higher temperature (75 ^{o}C), increase in the amount of catalyst concentration provides more active sites for the reaction to occur, thereby leading to higher FFA conversion yield and at catalyst concentration of 9 wt%, there is significant increase in FFA conversion yield across various levels of temperatures. Therefore, additional catalyst concentrations may not be necessary if the temperature is high enough [59]. A heterogeneous catalyst derived from palm fruit brunch was used in this research to synthesize biodiesel from FFA and the optimal conditions of 4 wt% catalyst, methanol to oil molar ratio of 21:1 and the temperature of 60 ^{o}C for 3 h produced the highest yield of 88.5 % [60]. The temperature for the optimum biodiesel yields reported by Thusari & Babel [61] was 70 ^{o}C and 110 ^{o}C, and this was due to the two derived solid acid catalysts used and the yield was 88.7 and 88.5 % respectively. This shows that the lower temperature (70 ^{o}C) was still more effective than the higher temperature (110 ^{o}C).

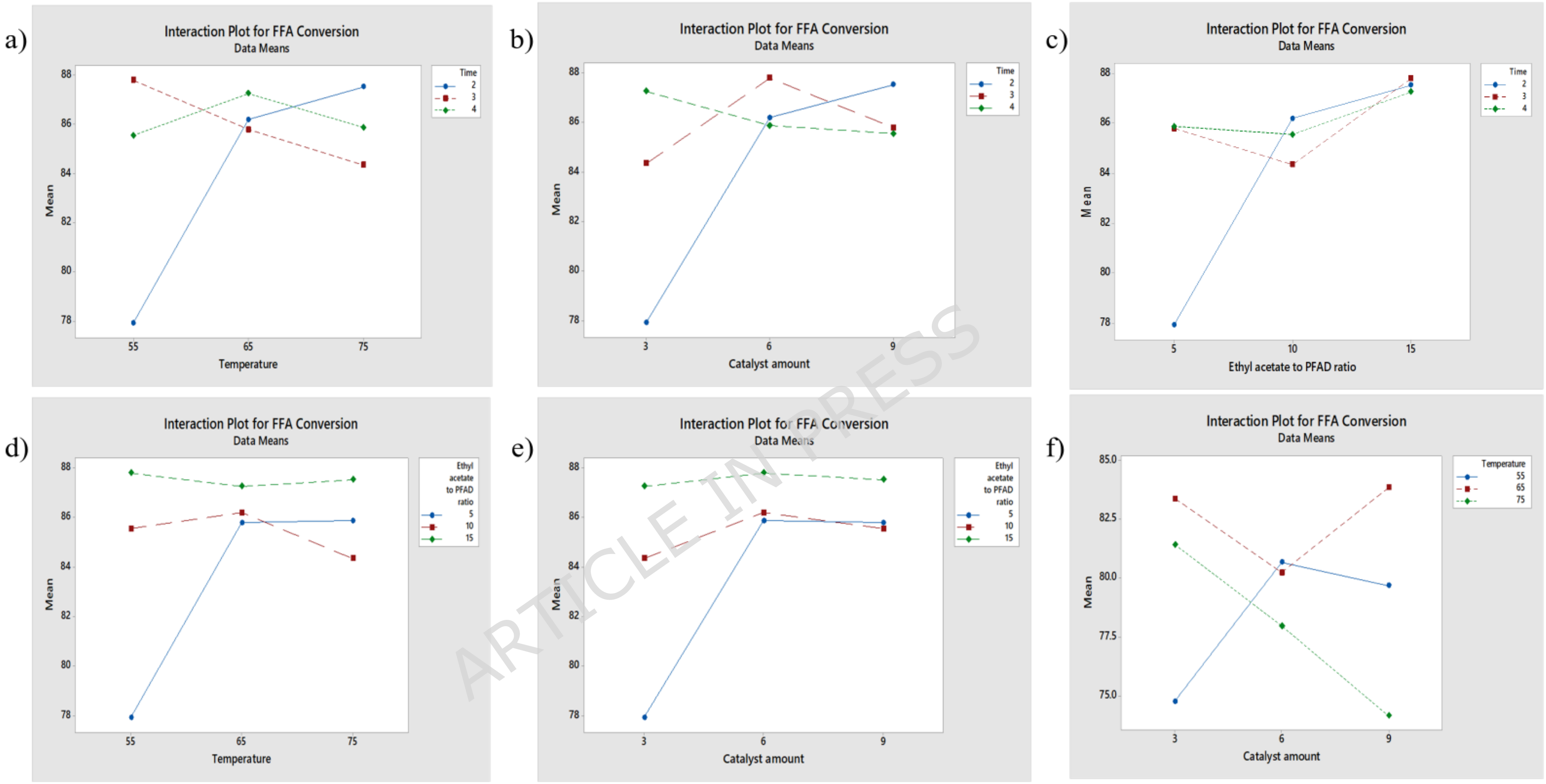

Fig. 3: Interaction plot of PFAD FFA conversion between (**a**) time and temperature, (**b**) time and catalyst amount, (**c**) time and ethyl acetate to PFAD ratio, (**d**) ethyl acetate to PFAD ratio and temperature, (**e**) ethyl acetate to PFAD ratio and catalyst amount, (**f**) temperature and catalyst amount

Validation of predicted FFA conversion through optimized reaction conditions

This research used Minitab 19® software to optimize the reaction condition for FFA conversion using PFAD as the waste feedstock with ethyl acetate. The software predicted a signal-to-noise ratio (SNR_O) which was used to calculate a predicted maximum FFA conversion yield with the mathematical equation (1) which was also validated through experimental results.

$$Y_o = 10^{\frac{SNR_O}{20}} \tag{1}$$

Where SNR_O is the SNR for optimized reaction condition, Y_O is the predicted maximum FFA conversion yield. When the optimal levels of each reaction parameter were input into the software, it predicted SNR_O value of 87.74 %. Three experimental trials were conducted using the esterification process under the same optimized reaction conditions. The FFA conversion yields from these trials were 90.00 %, 80.00 %, and 88.84 %, with an average yield of 86.28 %. The slight difference between the predicted and experimental yields is likely due to external variables affecting the process.

Proposed mechanism of esterification reaction of FFA in PFAD with ethyl acetate

The sulphuric acid acts as a proton donor on the carbonyl oxygen of the free fatty acid because it is a strong acid, thereby protonating the carbonyl oxygen. This increases the electrophilicity of the carbonyl carbon, making it more susceptible to attack by nucleophile. Ethyl acetate acts as a nucleophile, attacking the activated carbonyl carbon of the protonated free fatty acid which leads to the formation of a tetrahedral intermediate as shown in Fig. 4. This intermediate undergoes rearrangement and transferring a proton, leading to the formation of the fatty acid ethyl ester and elimination of acetic acid.

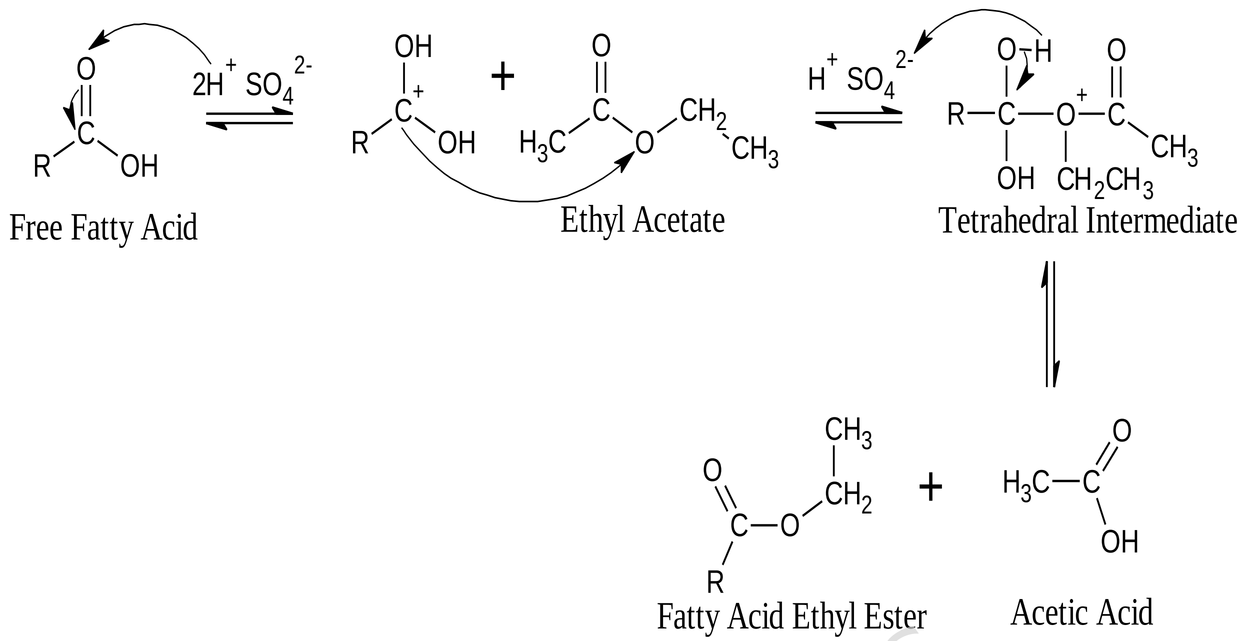

Fig. 4: Proposed mechanism of esterification reaction of FFA in PFAD with ethyl acetate

Comparison of esterification of PFAD with different catalysts and methylating agents

Previous studies on the use of palm fatty acid distillate with different catalysts and methylating agents under different reaction conditions for the production of biodiesel in comparison with this research are shown in Table 5. From this table, it was observed that most research were carried out using methanol and dimethyl carbonate with different catalysts for esterification of PFAD and they had relatively high yield. However, there are no research on the use of ethyl acetate with PFAD through esterification reaction. Therefore, the FFA conversion yield obtained in this research confirmed the feasibility of ethyl acetate with palm fatty acid distillate.

Table 5: Recent comparative review on esterification of PFAD with different catalysts and methylating agents

Methylating Agents	**Catalysts**	**Time (h)**	**Catalyst amount (wt%)**	**Temperature (°C)**	**Methylating agent ratio**	**FAME yield/FFA conversion (%)**	**References**
Methanol	Sulphonated CaO from Waste Angel Shell	3	5	80	15	98	[62]
Methanol	Sulfuric acid	0.15	1.834	121	3.71	97.1	[63]
Dimethyl carbonate (DMC)	Catalyst derived from spent bleaching clay	4	10	100	10	93.18	[64]
Methanol	Onion Peel (ACL)-(OPT)-SO3H	3	5	80	15	98.9	[50]
Methanol	Garlic Peel-ASB-(OPT)-SO_3H	3	6	99.85	15	94.4	[47]
Methanol	Rambutan seed (RS-SO_3H) catalyst	1.16	2.2	83.7	19	93.7	[14]
Ethyl acetate	Sulfuric acid	4	6	65	15	86.28	This study

Conclusion

This research successfully investigated the synthesis of biodiesel through the esterification of free fatty acids in PFAD using homogeneous sulfuric acid as a catalyst and ethyl acetate as the methylating agent. From this research, the characterization of PFAD feedstock confirmed its suitability with a high FFA value of 91.78±0.62 % and acid value of 234.82±1.65 mg KOH/g which also helps in waste management. The Taguchi orthogonal design revealed the percentage contribution of each parameter on FFA conversion whereby the ethyl acetate to PFAD molar ratio had the most significant effect of 28.10 %, followed by catalyst amount of 26.20 %, reaction temperature of 23.11 % and reaction time had the least effect of 22.59 %. Contour and interaction plots illustrated the complex relationships and influences of these parameters. The maximum FFA conversion yield of 87.74 % was predicted by the Minitab 19® software under optimal conditions. Experimental validation trials under these conditions yielded an average FFA conversion of 86.28 %, demonstrating good agreement with the predicted value.

However, this research found limited literature on the esterification reaction between ethyl acetate and PFAD using Taguchi method, thereby highlighting the novelty of this study. The feasibility of this research provided a sustainable, cost-effective method for converting a waste industrial by-product into biodiesel, which also contributes significantly to both waste management which aligns with SDG-12 (Responsible consumption and production) and the broader goals of renewable energy production, thereby reducing carbon emission into the environment which aligns with SDG-7 (Affordable and clean energy). Compared to traditional methods, this route is a glycerol-free process (using ethyl-acetate) addressing glycerol disposal issues, and yields valuable acetic acid as by-product and reducing reliance on food-competing feedstocks. This research offers practical industrial relevance as it demonstrates a scalable, low-cost, and sustainable process for biodiesel production using PFAD. The key industrial benefits which include conversion of PFAD waste into value-added biodiesel, aiding waste minimization and fewer experimental runs through Taguchi optimization. The Taguchi method employed, was able to reduce time and costs by minimizing trials while also providing reproducibility and scalability in industrial processes. This research suggests the use of PFAD with heterogeneous catalyst in order to test further effectiveness of the samples with ethyl acetate and enhance the green chemistry potential of this process. Future studies should focus on catalyst recovery and reusability tests, kinetic modeling of PFAD-ethyl acetate esterification, and techno-economic evaluation for industrial scale-up.

Materials and methods

Materials and reagents

Ethyl acetate (99 %) was purchased from Sigma Aldrich, and sulfuric acid was purchased from BDH Chemical Ltd (Poole England). Potassium hydroxide pellets (KOH), Sodium thiosulfate ($Na_2S_2O_3$), potassium iodide (KI), Ethanol (C_2H_5OH), Chloroform ($CHCl_3$), Acetic acid (CH_3COOH), Hanus iodine solution, and Starch soluble were obtained. The PFAD sample was sourced from commercial palm oil refinery in Benin, Edo State, Nigeria. Prior to use, the sample was characterized to verify its suitability for the production of biodiesel. Batch variability was assessed via triplicate of the physicochemical analysis.

Physicochemical parameters of PFAD feedstock

The physicochemical parameters determined include: free fatty acid value, acid value, peroxide value, saponification value, and iodine value.

Determination of Free Fatty Acid value (FFA)

The procedure described by Febrianto et al. [65] was followed in determining the free fatty acid value. The PFAD (3 g) was weighed and put into an empty 250-millilitre Elenmeyer flask. Then 30 ml of ethanol was added and 2 ml of phenolphthalein indicator was introduced into the sample. The solution was titrated with NaOH (0.1N) and the titrant's volume was noted. Three titrations were carried out for the sample. The following formula was used to determine the sample's free fatty acid value:

$$\%\ \text{Free fatty acid} = \frac{\mathrm{V} \times \mathrm{N} \times \mathrm{BM}}{\mathrm{m} \times 1000} \qquad (2)$$

Where: V= volume of NaOH titrated (mL), N= Normality of NaOH, BM = molecular weight of fatty acid (gram) and m = Mass of oil sample.

Determination of acid value

Using the procedure outlined by [37], the acid value was determined. 100 ml of ethanol was added to each 1 g of PFAD, which was then weighed and dissolved in the flask. A 0.1 N potassium hydroxide solution (KOH) was used to titrate two drops of phenolphthalein indicator to the pink end point. The volume of KOH used was noted. The sample underwent three titrations and the following formula was used to determine each sample's acid value:

$$\text{Acid value} = \frac{56.1 \times \mathrm{v} \times \mathrm{c}}{\mathrm{m}} \qquad (3)$$

Where: 56.1 = Equivalent weight of KOH, V = Volume of KOH titrated (ml), C = Concentration of KOH (0.1N) and m = Mass of the oil sample (grams).

Determination of iodine value

The Hanus iodine solution method was used to determine the iodine value [66]. The PFAD (0.25 g) was weighed accurately into a conical flask of 500 ml and distillated in 10 ml of chloroform. A measuring cylinder was used to add 25 ml Hanus iodine solution and allowed to stand in dark for 30 minutes, shaking occasionally for an accurate result. Then 10 ml of 15 % KI solution was added, after which it was shaked thoroughly, and 100 ml fresh boiled and cooled H_2O was added. The solution was then titrated with standard 0.1 N $Na_2S_2O_3$, which was added gradually while shaking continuously, until yellow solution became nearly colorless. Afterwards, 0.5 ml of starch indicator was added and it was titrated continuously till the blue color vanished completely tending to the end of reaction, the mixture was shaken vigorously, to ensure any remaining iodine in the chloroform solution was absorbed by the KI solution. The same procedure was carried out without the oil sample and this was referred to as blank test. The sample underwent three titrations, and the iodine value was calculated using the formula below:

$$\text{Iodine value} = \frac{(B-S)\times N \times 12.69}{Wt.\ of\ sample} \qquad (4)$$

Where: B = volume of blank solution (ml), S = volume of standard $Na_2S_2O_3$ (ml) and N = Normality of $Na_2S_2O_3$.

Determination of saponification value

The method described by Triyasmono et al. [67] was used to calculate the saponification value. The PFAD (5 g) was weighed into 50 ml of alcoholic hydroxide (KOH + ethanol) in a round-bottom flask. A few drops of the phenolphthalein indicator was added to the content in the round bottom flask and 0.5 N HCl was used to titrate the solution. The disappearance of the pink color indicates the saponification value. The blank determination procedure was carried out in the same way without adding the sample. The following formula was used to determine the saponification value for the sample:

$$\text{Saponification value} = \frac{28.05 \times (\mathrm{Vb}-\mathrm{Vs})}{Ws} \qquad (5)$$

Where: V_b = Volume of standard HCl solution used for blank test (ml), V_s = Volume of standard HCl solution used for sample (ml) and W_s = Weight of oil sample

Determination of peroxide value

The methodology outlined by Putri et al. [68] was used to calculate the peroxide value. A conical flask containing 10 g of PFAD was filled with 30 ml of a solvent mixture of glacial acetic acid and chloroform. After a vigorous shake, clockwise and counterclockwise, 1 ml of saturated KI was added, followed by the addition of 30 ml of distilled water and vigorously shaking it for a minute. Then 0.5 ml of starch indicator was added, and the mixture was titrated using a 0.01 N $Na_2S_2O_3$ solution. The mixture was then shaked vigorously until the black color turns white to initiate the reaction. Alongside the oil samples, a blank was made. The sample's peroxide value was determined using the formula below:

$$\text{Peroxide value} = \frac{\mathrm{V} \times \mathrm{N} \times 1000}{Ws} \qquad (6)$$

Where: V = Volume of standard $Na_2S_2O_3$ (ml), N = Normality of $Na_2S_2O_3$ and Ws is the weight of oil.

Esterification of PFAD using ethyl acetate

Initial experimental studies were conducted to produce biodiesel from PFAD esterification using ethyl acetate, focusing on one factor at a time. Key parameters including: ethyl acetate to PFAD molar ratio, reaction temperature, catalyst concentration and reaction time were studied. The esterification was carried out using 3 g of PFAD with required amounts of ethyl acetate, and the catalyst (sulfuric acid) was mixed inside a 50 ml round bottom flask. The round bottom flask was connected to a condenser, which was placed on a hot plate. The reaction was then done at the specified temperature for a particular reaction time at a stirring speed of 1000 rpm. Each experiment was done three times, and the average was calculated. The product was then prepared for analysis [69].

The mixture was allowed to settle and the biodiesel layer was separated from the acetic acid layer (containing the sulfuric acid catalyst and water from any side reactions). The biodiesel was then washed with warm distilled water (50 °C) three times to remove residual catalyst and acetic acid, dried over anhydrous sodium sulfate, and filtered. No significant phase-separation difficulty was encountered due to the immiscibility of biodiesel and aqueous fractions [70]. After the esterification reaction, the reaction mixture was subjected to vacuum distillation at 75 °C to remove and recover unreacted ethyl acetate. The recovered solvent was collected and reused in subsequent reactions to enhance process economics and reduce environmental impact [21].

FAME product analysis

This was used to determine the amount of FFA present in the feedstock that was converted. The percentage of FFA conversion was then calculated using equation (7) below:

$$\text{FFA Conversion (\%)} = \frac{FFAs - FFAf}{FFAs} \times 100 \qquad (7)$$

Where FFA_s is the FFA value of PFAD or SODD feedstock and

FFA_f is the FFA value of FAME product

This was determined according to the official standard method of AOCS [64].

Taguchi orthogonal design

The orthogonal arrays determined the necessary number of experiments and reaction conditions; choosing the suitable orthogonal array depend on the parameters and their variability levels. The minimum required experiments N was determined by the number of levels (L) and control parameters (P) as indicated in equation (8) below [71];

$$N = (L-1)\,P+1 \qquad (8)$$

This research used the L9 orthogonal array, and statistical analysis was carried out using Minitab 19® software.

Selection of control parameters and level

Experimental studies were conducted initially to investigate the effect of various parameters on use of PFAD with ethyl acetate for biodiesel production. These studies focused on one factor at a time. Four important parameters at three separate levels were used in this study. The required number of experimental runs was determined using equation (8), resulting in 9 runs; which made it correspond to the L9 orthogonal array. To reduce errors, each experimental run was repeated three times.

Signal to Noise Ratio (SNR) and Analysis of Variance (ANOVA)

Based on the anticipated objective, the Taguchi technique normally employs three different signal-to-noise ratios (SNRs). These three SNRs are: Larger-the-better (LTB), Smaller-the-better (STB), and Nominal-the-better (NTB) for maximization, minimization and normalization problems, respectively, and are calculated using equations (9) to (11)

$$\text{Larger the better — SNR}_i = -10 log \frac{1}{n}\left(\sum_{j=1}^{n} \frac{1}{y_j^2}\right) \qquad (9)$$

$$\text{Smaller the better —SNR}_i = -10 log \frac{1}{n}\left(\sum_{j=1}^{n} \frac{y_j^2}{n}\right) \qquad (10)$$

Nominal the better— $\mathrm{SNR}_i = 10 \log\left(\frac{\bar{y}_i^2}{S_i^2}\right)$ (11)

Where: $y_i = \frac{1}{n}\left(\sum_{j=1}^{n} y_{ij}\right)$ (12)

$S_i^2 = \frac{1}{n-1}\left(\sum_{j=1}^{n} y_{ij} - \bar{y}_i\right)$ (13)

y_i = mean yield value, S_i^2= variance, j = trial number, n = number of experimental trials, and i = experiment number.

The LTB model was used in this work because the primary aim was to achieve optimized conditions for the reaction in order to obtain the highest FFA conversion yield from PFAD esterification using ethyl acetate. The optimized reaction conditions aligned with the highest signal-to-noise ratio (SNR) level for each parameter. However, relying solely on SNR did not explicitly identify the specific parameter influencing FFA conversion yield and the magnitude of each parameter's impact. Therefore, a statistical analysis of the data variance was carried out to determine the contribution percentage of each parameter using equation (14):

% Contribution factor = $\frac{SS_K}{SS_T} X\ 100$ (14)

$SS_K = \sum_{j=1}^{3} n[(\ SNR_L)_{kj} - \ SNR_T]^2$ (15)

$SS_T = \sum_{i=1}^{9} (SNR_I - SNR_T)^2$ (16)

where SS_K = Sum of squares for the kth factor

SS_T = Total number of sum of squares of all parameters

SNRL= Level mean signal-to-noise ratio

n= number of experiments at level 'j' of factor 'k'.

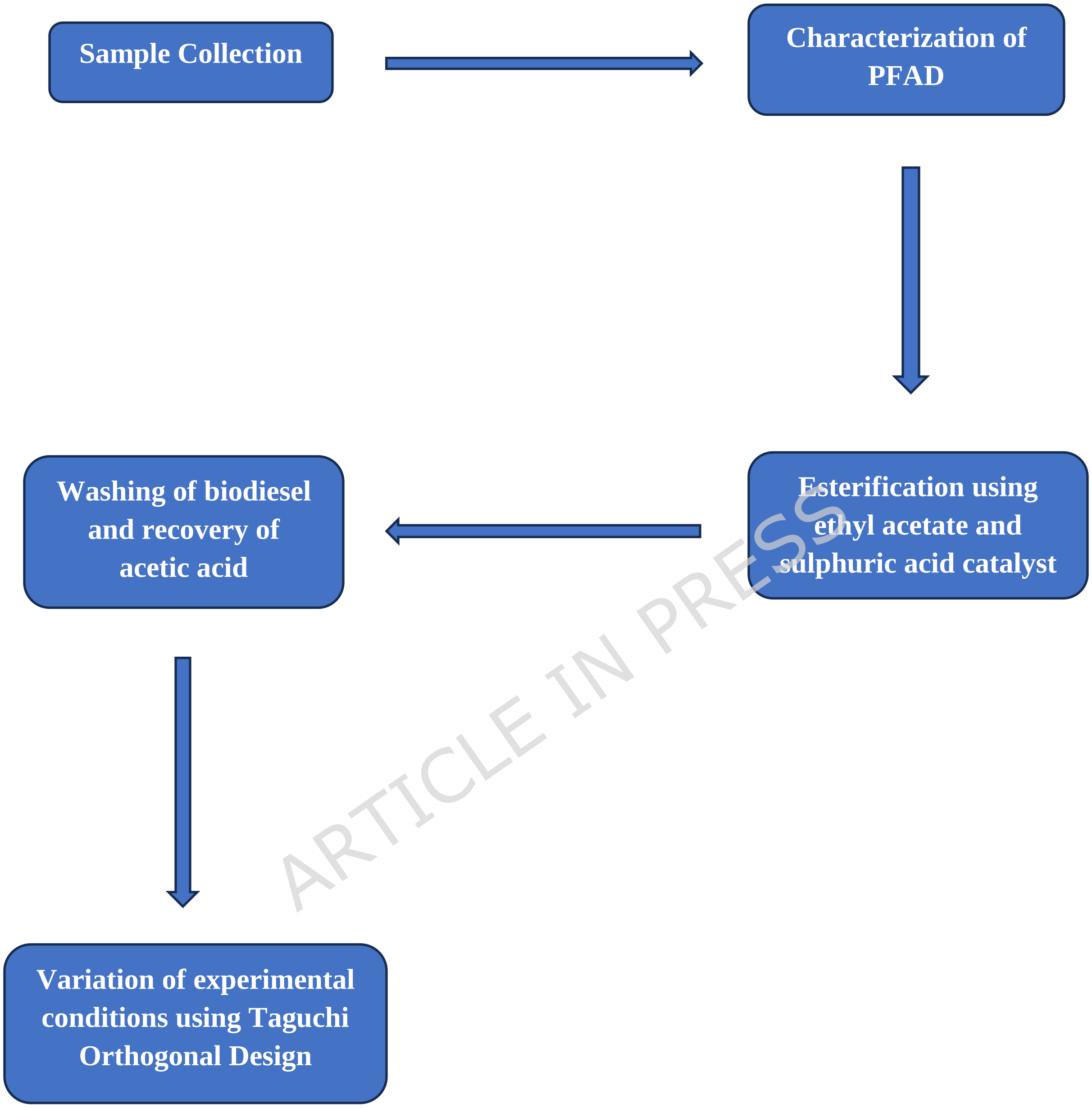

Fig. 5: Flow diagram of esterification reaction of FFA in PFAD with ethyl acetate

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Ethics declarations

Competing interests

The authors have declared no competing interest present in this research.

Data availability

All data generated or analysed during this study are included in this published article

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